DK 00/00495
10/070558

Kongeriget Danmark

Patent application No.: PA 1999 01828
Date of filing: 20 December 1999
Applicant: Niels Janniksen Bjerrum
Rådhusvej 59
DK-2920 Charlottenlund

See more Applicants mentioned in attached copy.

The attached photocopy is a true copy of the following document:

- The specification, abstract, claims and figures as filed with the application on the filing date indicated above.



Patent- og
Varemærkestyrelsen
Erhvervsministeriet

TAASTRUP 25 September 2000

Lizzi Vester
Head of Section

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Ansøgere fortsat

Ansøger (fulde navn og adresse):

Li Qingfeng
Bogtrykkervej 22 st. tv.
2400 Kbh. NV.

Telefon: 35 855888

Telefax:

Ansøger (fulde navn og adresse):

Hans Aage Hjuler
Dreyersvej 30
2960 Rungsted Kyst

Telefon: 45 863105

Telefax: 45 863157

Opfindere fortsat

Opfinder (fornavn, efternavn, adresse):

Hans Aage Hjuler
Dreyersvej 30
2960 Rungsted Kyst

Opfinder (fornavn, efternavn, adresse):

Opfinder (fornavn, efternavn, adresse):

Opfinder (fornavn, efternavn, adresse):

Prioritetspåstande fortsat

Dato	Land	Nr.
Dato	Land	Nr.
Dato	Land	Nr.
Dato	Land	Nr.
Dato	Land	Nr.
Dato	Land	Nr.

Modtaget
20 DEC. 1999
PVS

Danish Patent Application

Title: Blend Polymer Electrolytes for Fuel Cells

Inventors: Niels J. Bjerrum, Li Qingfeng, Hans Aage Hjuler

5

Abstract

Blend polymer electrolyte membranes based on PBI and various thermoplastic polymers have been developed for high temperature polymer electrolyte fuel cells. Miscible blends were used for solution casting of polymer membranes. High conductivity and enhanced mechanical strength were obtained for the blend polymer electrolytes. Corresponding technologies for gas diffusion electrode and membrane-electrode assembly fabrication were invented. The polymer electrolyte fuel cell based on developed blend membrane and gas diffusion electrodes operates at temperatures up to 200°C.

10

15

BACKGROUND OF THE INVENTION

1. TECHNICAL FIELD

The present invention is directed to polymer electrolyte membrane fuel cells based on blends of PBI and thermoplastic polymers. The fuel cell operates at temperatures up to 200°C with hydrogen fuel containing at least 3 vol% carbon monoxide.

2. BACKGROUND OF THE INVENTION

The currently well developed technology of polymer electrolyte membrane (PEM) fuel cells is based on perfluorosulfonic acid polymer membranes (e.g. Nafion®) as electrolyte. The conductivity of this polymer membrane is dependent on the presence of water to solvate the protons from the sulfonic acid groups. Consequently the operational temperature is limited to be below 100°C, typically 60-95°C, at atmospheric pressure. At higher temperatures, the conductivity reduces dramatically since water is lost. By means of a pressurized system the operational temperature can be extended but at the expense of overall system efficiency, size and weight. For an operation around 200°C, however, the pressure required will be too high to be of any practical use.

This is unfortunate because the use of a polymer electrolyte membrane at temperatures higher than 100°C is desirable in several ways. The electrode kinetics will be enhanced and the catalytic activity will be increased at higher temperatures for both electrodes. Another benefit is the reduced poisoning effect of the catalysts by fuel impurities e.g. carbon monoxide, which have been known to be very temperature-dependent, since CO adsorption is less pronounced with increasing temperature. At 80°C, the typical operational temperature of a Nafion-based polymer membrane electrolyte fuel cell, for example, a CO content as low as 20-50 ppm in the fuel steam will result in a significant loss in the cell performance. As a consequence very pure hydrogen is needed for operation of polymer electrolyte fuel cells.

For applications as a power system for automobiles, liquid fuels such as methanol are more favorable. The current usage of methanol in PEM fuel cells is indirect, i.e., via a fuel processing system to convert the fuel into free hydrogen, CO₂ and a small amount of CO. CO needs to be removed down to 10 ppm level by means of a water-gas shift reactor followed by a preferential oxidizer and/or a membrane separator. For a small dynamic load as in a vehicle, the main challenge for the on-board processing system is the complexity, which not only requires increased cost, size and volume, but also reduces the start-up time and transient response capacity of the system. Such a fuel processing system generally covers 40-50% of the cost of a fuel cell power stack. This can be decisively simplified by introducing a CO tolerant polymer membrane electrolyte fuel cell.

Direct usage of methanol will be the ultimate option, since the dispensation with the complicated gas processors for reforming and CO removal is very much desired especially

for automobile applications. However the technology is at present far from satisfaction. One of the major challenges is the anodic catalyst. Although Pt/Ru alloy is still recognized as the best, it is not sufficiently active, resulting in high anodic overpotential loss (ca. 350 mV compared to ca. 50 mV for hydrogen) and requiring high catalyst loading of electrode (3.0-8.0 mg/cm²). The insufficient activity of the anode catalyst is due to the slow kinetics of methanol oxidation and the strong poisoning effect of the intermediate species (CO) from the methanol oxidation, both expected to be considerably improved by increasing the operational temperature of DMFC.

The newest technology in the field is the development of temperature-resistant polymer membranes, which allow the PEMFC operation to be in a temperature range up to 200°C. Based on polybenzimidazoles (PBI), the new polymer membranes exhibit excellent thermal stability, high chemical resistance, and outstandingly high glass transition temperature. When sulfonated, phosphonated, or doped with an acid, the polymer membrane becomes a proton conductor at temperatures up to 200°C. This polymer membrane can be used as electrolyte for PEM fuel cells with various types of fuels such as hydrogen, methanol, trimethoxymethane, and formic acid. Besides these, this polymer electrolyte membrane has also been used for hydrogen sensors, electrochemical capacitor and other electrochemical cells (see for example *US patent 5,688,613*). Related techniques for fabricating gas diffusion electrodes and membrane-electrode assemblies have also been disclosed (*Danish patent application PA199901274, 1999*).

3. SUMMARY OF THE INVENTION

The present invention provides blend polymer membranes as electrolyte for high temperature PEM fuel cells. The blend polymer electrolyte exhibits high ionic conductivity, enhanced mechanical properties at operational temperatures, and easiness to handle during preparation. Related techniques have been developed for preparing gas diffusion electrodes and membrane-electrode assemblies for polymer electrolyte fuel cells operating at temperatures up to 200°C. Gas diffusion electrodes using the blend polymer as binder were prepared by a tape-casting method. The gas diffusion electrode is then doped with a mixture of acids. The membrane-electrode assemblies were then fabricated by hot-pressing the doped electrode onto the acid-doped polymer membrane. The assemblies prepared in this way give good performance and high tolerance to the fuel impurities e.g., carbon monoxide.

4. BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1. Doping level of PBI/SPSU blend membranes as a function of acid concentration at room temperature. Sulfonation degree of PSU was 36%. The PBI/SPSU blend compositions are 50-50, 62.5-37.5, 75-25, 87.5-12.5, and 100-0 mol%.

FIG.2. Ionic conductivity of PBI/SPSU blend membranes as a function of doping level at temperature of 25°C and relative humidity of 80%. Sulfonation degree of PSU was 36%. The PBI/SPSU blend compositions are 50-50, 62.5-37.5, 75-25, 87.5-12.5, and 100-0 mol%.

FIG.3. Mechanical strength of PBI/SPSU blend membranes as a function of doping level at temperature of 25°C. Sulfonation degree of PSU was 36%. The PBI/SPSU blend compositions are 50-50, 62.5-37.5, 75-25, 87.5-12.5, and 100-0 mol%.

FIG.4. Mechanical strength of PBI/SPSU blend membranes as a function of doping level at temperature of 150°C. Sulfonation degree of PSU was 36%. The PBI/SPSU blend compositions are 50-50, 62.5-37.5, 75-25, 87.5-12.5, and 100-0 mol%.

FIG.5. Cell voltage versus current density curves of the high temperature polymer membrane electrolyte fuel cell at 190°C. Electrodes with a platinum loading of 0.45 mg/cm²; the PBI/SPSU membrane at doping level of 4.5/1; oxygen at 1 bar and 200 ml/min; hydrogen and hydrogen containing 3% CO at 1 bar and 160 ml/min.

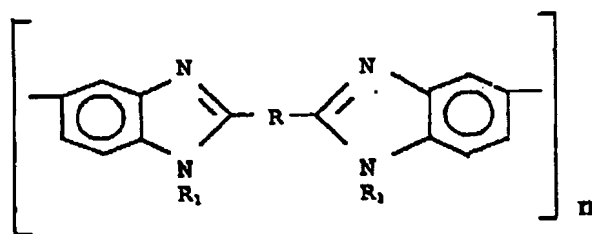
FIG.6. Cell power density versus current density curves at 190°C. Electrodes with a platinum loading of 0.45 mg/cm²; the PBI/SPSU membrane at doping level of 4.5/1; oxygen at 1 bar and 200 ml/min; hydrogen and hydrogen containing 3% CO at 1 bar and 160 ml/min.

5. DETAILED DESCRIPTION OF THE INVENTION

The invention relates to the idea and technique for preparing high performance blend polymer membranes and corresponding gas diffusion electrodes, from which membrane-electrode assemblies are fabricated for high temperature polymer membrane fuel cells.

Temperature-resistant polymer membrane electrolytes

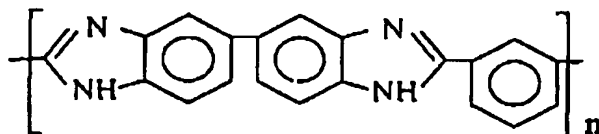
It is well known that polymers containing basic groups can form complexes with stable acid or polymers containing acidic groups. This provides an alternative to the polymer membrane electrolytes for both PEM and other applications. Among these basic polymer families are polypyrimidines, polyimidazole, polybenzoxazoles, and most preferred polybenzimidazoles with a chemical structure shown below (Scheme 1):



Scheme 1. Polybenzimidazoles

where the functional groups R and R₁ can be various chains such as alkane-chain, fluoro alkane chain, and others. For enhanced thermal stability, a molecule consisting only of

aromatic groups is preferred, for example, poly(2,2'-m-(phenylene)-5,5''-bibenzimidazole (PBI, Celazole®), provided by Celanese Acetate (Scheme 2):



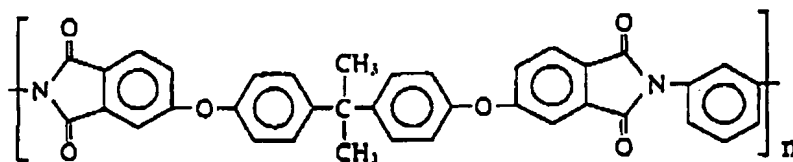
Scheme 2. Poly(2,2'-m-(phenylene)-5,5''-bibenzimidazole

This PBI is an amorphous thermoplastic polymer with a glass transition temperature of 425-436°C. Chemically the PBI possesses both donor and acceptor hydrogen-bonding sites which are capable to participate in specific interactions. In the presence of acids or bases, a PBI polycation can be formed resulting in acid or base neutralization in the formation of a salt with the imidazole ring structure. An electrolyte active species dispersed within the polymer structure is a necessity for proton conduction. The proton conducting active species can be either an acid (such as phosphoric acid H_3PO_4 , sulfuric acid H_2SO_4 , hydrochloric acid HCl , nitric acid HNO_3 , and their combinations) or a base (such as metal hydroxide KOH , $NaOH$, $LiOH$, and their combinations). For PEM applications, the most preferred polymer electrolyte is prepared from poly(2,2'-m-(phenylene)-5,5''-bibenzimidazole and phosphoric acid.

The conductivity of the combined PBI/H_3PO_4 membrane electrolyte is found to be dependent on the acid-doping level. At high doping levels proton conductivity as high as 0.13 S/cm is obtained at temperature of 150°C and relative humidity of 80%. However, the high doping level results in a significant reduction in the mechanical strength of the membrane. By increasing the doping level from 4 to 10, for example, the tensile strength decreases from 220 to 60 kg/cm² at 150°C.

It is widely accepted that miscible polymer blends and copolymerization offer complementary routes to polymer systems with tailored properties. PBI forms miscible blends with a broad range of thermoplastics, due to the hydrogen bonding effect and interaction between the amine groups of PBI and carbonyl groups of the thermoplastic polymers. Examples of thermoplastics, which are miscible with polybenzimidazole, include polyimides (PI), polyamides (PA), polyamideimide (PAI), polyetherimides (PEI), polyarylate (PAr), and poly(4-vinyl pyridine) (PVPy).

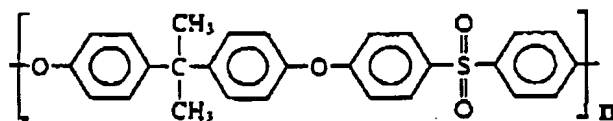
Taking polyetherimides (PEI) as an example, PEI is an amorphous high performance polymer, characterized by thermal and chemical resistance and excellent mechanical properties. The base polymer has a transparent amber brown color and is manufactured by polycondensation. PEI has a transition temperature of 217-220°C with a chemical structure (Scheme 3):



Scheme 3. Polyetherimide

Concerning the mechanical properties PEI breaks at an elongation of 33%, while PBI at only 1.8-3.0%. The polymer blends are therefore expected to exhibit improved mechanical properties [See *Specialty Polymers*, ed. R. W. Dyson, Blackie Academic & Professional, 1998].

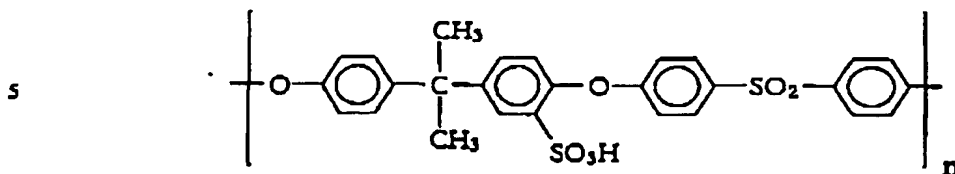
Another group of thermoplastics are immiscible with polybenzimidazoles. An example is polysulfone (PSU), which has a transition temperature of 190°C and exhibit excellent mechanical properties with a chemical structure (Scheme 4):



Scheme 4. Polysulfone (PSU)

The elongation at break for PSU, for example, is reported to be 50-100%, compared again to 1.8-3.0% for PBI [See *Specialty Polymers*, ed. R. W. Dyson, Blackie Academic & Professional, 1998]. As T. S. Chung reported [*Polym. Eng. Sci.*, 34, 428, (1994)], blends of PSU and PBI forms high performance fibers despite the immiscibility of the two polymers.

Ionomers, defined as polymers containing a small amount of bonded ionic groups, are generally promising polymers for promoting miscibility with various types of polymers. The ionic functional groups are believed to facilitate specific interactions such as hydrogen bonding. Sulfonation of PSU has been reported [see *Polym. Eng. Sci.*, 33, 1042, (1993)], making the polymer bear functional groups and exhibit high glass transition temperatures, see Scheme 5.



Scheme 5. Sulfonation of PSU

15 It is naturally enough that the presence of sulfonate groups are expected to improve the ionic conductivity of the polymer membrane electrolytes. It is demonstrated in the present invention that the sulfonated polysulfone (SPSU) forms a miscible blend with PBI due to participation of functional groups in hydrogen-bonding interactions. This allows a simple solution casting of the blend polymer membranes.

Preparation of PBI blends

20 The polymer powder (-100 mesh), supplied by Celanese Acetate, was first mixed with dimethylacetamide (DMAc) and contained in a stainless steel bomb reactor. Lithium chloride was added as a stabilizer. Oxygen was excluded from the bomb by bubbling argon through the mixture solution. The bomb reactor was then closed and placed in a rotating oven at 250°C for 3-5 hours. The solution was then diluted with DMAc for the membrane casting.

25 Sulfonated PSU in form of sodium salt was prepared by using chlorosulfonic acid as a sulfonated agent in a dichloroethane solution. Solution of sulfonated PSU was made by mixing the polymer with dimethylacetamide (DMAc) under stirring at room temperatures.

30 Polyetherimide (Utem 1000), provided by GE Plastics, was first dried under vacuum, and then dissolved in dimethylacetamide under stirring at room temperatures.

35 Blends of PBI/SPSU and PBI/PEI were obtained by mixing the corresponding polymer solutions in a desired ratio. A certain amount of the mixture solution was poured into a glass dish. The major part of the solvent was evaporated in a ventilated oven at 80-120°C. The membranes were then washed with distilled water at 80°C to remove the residual solvent and stabilizing salts, and finally dried at 190°C.

Doping of PBI blend membranes

40 The PBI/SPSU blend membranes were doped with an acid of various concentrations. The acid can be phosphoric acid or sulfuric acid. Doping levels, defined as the molar ratio of the doping acid to the average value of PBI and SPSU (repeating units), depend on the concentration of the acid, temperature, and duration.

45

Fig. 1 shows doping levels of the polymer blend membranes as a function of phosphoric acid concentration at room temperatures. As a comparison, tests of pure PBI membranes were also included. Pure PBI membranes are easy to be doped.

The PBI/PEI blend membranes were doped with an acid of various concentrations. A 75%PBI-25%PEI blend membrane, for example, was doped with 75% phosphoric acid. After reaching saturation, the doping level was found to be around 660 mol%.

Conductivity measurements

Ionic conductivity of the blend polymer membrane electrolytes was measured by means of a four probe cell. As shown in Fig. 2, the PBI/SPSU blend polymer membranes exhibit much higher conductivity than pure PBI membranes. At a doping level of 600 mol% H_3PO_4 , for example, the conductivity of pure PBI membranes is around 0.014 S/cm at temperature of 25°C and relative humidity of 80%, while that of 50-50 mol% PBI-SPSU blend polymer membranes is about 0.052 S/cm. The functional groups in the sulfonated PSU apparently takes part in the ionic conduction and therefore a high conductivity of blend polymer membranes is therefore expected.

For PBI/PEI blend membranes, the conductivity as a function of doping level is found to be very close to that pure PBI. As an example, a 75%PBI-25%PEI blend membrane doped at a level of 660 mol% H_3PO_4 exhibits a conductivity from 0.013 to 0.017 S/cm.

Tensile strength measurements

For pure PBI membranes, high doping levels result in a reduction in the mechanical strength, especially at high temperatures. A proper doping level in a low range is consequently preferred, corresponding to a low electric conductivity. For the PBI-SPSU blend polymer membrane electrolytes, the mechanical strength was measured at both 25 and 150°C. Fig. 3 shows the results as a function of the membrane doping level at room temperatures. No improvement was observed for blend polymer membrane electrolytes. At 150°C, however, as shown in Fig. 4, the mechanical properties of membranes were much improved for blend polymer electrolytes. At a doping level about 600-660 mol% H_3PO_4 , for example, the tensile stress for pure PBI membranes is 42-61 kg/cm², while that for 50-50 mol% PBI-SPSU blends is as high as 75-92 kg/cm².

For pure PEI membrane, the tensile stress is found to be as high as 563-613 kg/cm² at 25°C and 413-438 kg/cm² at 150°C. A 75%PBI-25%PEI blend membrane doped at a level of 600-660 mol% H_3PO_4 exhibits a tensile stress of 201-220 kg/cm² at 25°C and 88-113 kg/cm² at 150°C, compared to a pure PBI membrane doped with 600-660 mol% H_3PO_4 , having a tensile stress of only 128-147 kg/cm² at 25°C and 42-61 kg/cm² at 150°C.

Gas diffusion electrodes

Chloroacids of noble metals from Group VIII of the periodic table, particularly platinum and ruthenium, were prepared. Different types of carbon black of high surface area (typically from 200 to 1000 m²/g), either graphited or non-graphited, can be used as supporting materials. With help of a surface agent, e.g., acetic acid, the metal ions were chemically reduced by a reducing agent selected from, among others, formic acid, formaldehyde, sodium borohydride, etc. The obtained carbon supported catalyst was then filtered and washed with distilled water and dried and ground into a fine powder. Alloying of metals can be prepared by using a mixture solution of desirable metal chloroacids.

Various fibrous carbon materials in form of paper or cloth can be used as the backing substrate. It is generally desirable that the materials have low electric resistance in the operational temperature range of a fuel cell. For convenience of tape-casting, carbon fibrous paper, for instance, Toray TGP-H-120, was preferred. The carbon material was first wet-proofed by immersing in a hydrophobic polymer dispersion, such as fluorinated ethylene propylene or polytetrafluoroethylene, and then dried and sintered at 360°C for 20 minutes. The loading of the hydrophobic polymer is controlled by changing the concentration of the dispersion.

A slurry of uncatalyzed carbon powder with 40% PTFE was prepared and applied on to the hydrophobic backing carbon substrate to form a supporting layer. After sintering at 360°C for 20 minutes, this layer is hydrophobic. In addition, this layer provides a smooth surface of tiny particles and therefore prevents the catalyst layer from cracking.

Carbon supported noble metal catalysts, with a weight ratio of the noble metal to carbon from 0.1 to 0.2, were mixed with a soluble polymer and applied to the top of the supporting layer on a wet-proofed carbon paper. The electrodes were then dried and sintered at 130 - 190°C for 30 - 180 minutes. It is important to remark that, when the PBI/SPSU blend polymer solution is used instead of pure polybenzimidazole solution, the porous catalyst layer is smooth without cracking. The loading of the blend polymer in the catalyst layer of electrodes is preferably around 0.5 - 1.5 mg/cm². The electrodes made in this way have a platinum loading of 0.2 - 0.8 mg/cm².

Membrane-electrode assemblies

The catalyst layer in the gas diffusion electrodes, as described above, contains the PBI/SPSU polymers. This polymer needs to be doped with an acid in order to achieve the protonic conductivity. This is done with a mixture of a nonvolatile acid and a volatile acid. The nonvolatile acid is the same acid as used for doping the membrane, i.e., either sulfuric acid or phosphoric acid. The volatile acid, e.g., trifluoroacetic acid or acetic acid, is used to facilitate the wetting of the dopant solution on the surface of the electrode. The amount is determined by the polymer content in the catalyst layer of the electrodes. A molar ratio of

the nonvolatile acid to the polymer content is preferred in a range from 5/1 to 20/1, and preferably from 10/1 to 15/1.

Assemblies from the doped electrodes and the doped polymer membranes were made by means of hot-press. Temperature, pressure and duration are critical parameters and a set of optimal parameters are found to be temperature 130-200°C, pressures of 0.3-1.5 bar/cm², and a duration of 5-30 minutes.

Single cell tests

A single test cell (5 cm²) has been built up to perform electrochemical characterizations of the membrane-electrode assemblies. Graphite plates with gas channels were used as the holder. Two aluminum end plates with attached heaters are used to clamp the graphite plates and collect current. Temperature is controlled by a controller. Fuel and oxidant gases were supplied by means of mass flow controllers. Performance curves were obtained by the current step potentiometry. Potential values at various current densities were then taken from chronopotentiometric curves when a steady state was reached.

It is well known that the Nafion-based membrane electrolyte usually has a large electro-osmotic drag number, i.e., water moves from the anode side to the cathode side during cell operation, resulting in the requirement of an intensive gas humidification to maintain an adequate membrane hydration. This, together with operational temperatures near the boiling point of water, makes the cell operation very critical with respect to both water and heat management.

The PBI based blend polymer membrane is found to have a water drag coefficient of virtually zero. This makes the high temperature PEM fuel cell possible to operate with no humidification of the reactive gases. The elimination of humidification substantially simplifies the construction and operation of the polymer fuel cell.

For evaluating the tolerance of the technology to fuel impurities, a mixture of 97 vol% hydrogen and 3 vol% carbon monoxide was pre-made. Mixed gas of other compositions was obtained by means of mass flow meters and controllers. It is found that the present technology can tolerate up to at least 3 vol% carbon monoxide in the hydrogen fuel, i.e., 20,000-30,000 ppm CO compared to 10-20 ppm CO for Nafion-based polymer electrolyte fuel cells at 80°C.

Example 1

3 wt% PBI solution in dimethylacetamide was mixed with 3 wt% sulfonated polysulfone in a weight ratio of 75 to 25. The polysulfone was sulfonated to a 44% degree by using chlorosulfonic acid as a sulfonated agent in a dichloroethane solution. After drying, the polymer membrane was washed with distilled water at 80°C to remove the residual solvent and stabilizing salts.

The membrane was thereafter immersed in phosphoric acid of concentration 80, 70, 60 and 50 wt%, respectively. After 8 days at room temperature, the membrane was doped at levels of 801, 550, 459, and 381 mol% H_3PO_4 , accordingly. At 25°C the ionic conductivity of the obtained blend membranes was found to be 0.054, 0.049, 0.031, and 0.020 S/cm, respectively.

Example 2

5 wt% PBI solution in dimethylacetamide was mixed with 5 wt% sulfonated polysulfone in a weight ratio of 50 to 50. The polysulfone was sulfonated to a 36% degree by using chlorosulfonic acid as a sulfonated agent in a dichloroethane solution. After drying, the polymer membrane was washed with distilled water at 80°C to remove the residual solvent and stabilizing salts.

The membrane was thereafter immersed in phosphoric acid of concentration 85, 75, and 65 wt%, respectively. After 10 days at room temperature, the membrane was doped at levels of 702, 467, and 381 mol% H_3PO_4 , accordingly. At 25°C the ionic conductivity of the membranes was found to be 0.056, 0.048, and 0.026 S/cm, respectively.

Example 3

10 wt% PBI solution in dimethylacetamide was mixed with 10 wt% polyetherimide in a weight ratio of 75 to 25. After drying, the polymer membrane was washed with distilled water at 80°C to remove the residual solvent and stabilizing salts.

The membrane was thereafter immersed in phosphoric acid of concentration 75 wt%. After 10 days at room temperature, the membrane was doped at a level of 660 mol% H_3PO_4 . At 25°C the ionic conductivity of the membranes was found to be 0.015 S/cm. The ionic conductivity of pure PBI membranes doped with about 660 mol% was 0.014 S/cm.

At a doping level of 660 mol% H_3PO_4 , the tensile stress at 150°C for pure PBI membranes was found to be 54 kg/cm², while that for 50-50 mol% PBI-SPSU blend membrane was found to be 87 kg/cm².

Example 4

The wet-proofed carbon backing substrate was coated with a carbon supporting layer (of 60 wt% carbon powder and 40 wt% polytetrafluoroethylene). This supporting layer is hydrophobic so that it allows access of reactive gases. As a bridge between the carbon paper backing and the catalyst layer this layer also prevents the electrode from serious cracking after drying and sintering.

The platinum chloroacid was first prepared by dissolution of metallic platinum in a mixture of concentrated nitric acid and hydrochloride acid. The platinum chloroacid was then mixed with carbon powder (Vulcan XC-72, Cabot). With help of surface active agents the noble

metal was chemically reduced on the surface of the carbon powder at 95°C. The obtained carbon-supported platinum catalyst (20 wt% Pt) was then filtered, washed with distilled water, dried, and finally ground into a fine powder.

5 A mixed polymer solution of PBI and SPSU with a weight ratio of 50 to 50 was used as binder for the catalyst layer. A slurry of 40 wt% Pt/C catalyst powder and 60 wt% mixed polymer solution was well mixed and applied on to the supporting layer of the carbon paper by tape-casting. The platinum loading in the catalyst layer was 0.45 mg/cm². After drying the electrode was impregnated with a mixed acid of 65 wt% phosphoric acid and 35 wt% trifluoroacetic acid.

10 An acid-doped blend polymer membrane of 50% PBI and 50% SPSU (sulfonation degree 36%) was used as the electrolyte. From the impregnated electrodes and acid-doped PBI membranes, a membrane-electrode assembly was made by hot-press. The assembly was then placed in a test cell. At 190°C with hydrogen and oxygen, a cell performance of current density 0.89 A/cm² at cell voltage of 0.5 V was obtained.

Example 5

20 The wet-proofed carbon backing substrate was coated with a carbon supporting layer (of 60 wt% carbon powder and 40 wt% polytetrafluoroethylene). This supporting layer is hydrophobic so that it allows access of reactive gases. As a bridge between the carbon paper backing and the catalyst layer this layer also prevents the electrode from serious cracking after drying and sintering.

25 The platinum chloroacid was first prepared by dissolution of metallic platinum in a mixture of concentrated nitric acid and hydrochloride acid. The platinum chloroacid was then mixed with carbon powder (Vulcan XC-72, Cabot). With help of surface active agents the noble metal was chemically reduced on the surface of the carbon powder at 95°C. The obtained carbon-supported platinum catalyst (20 wt% Pt) was then filtered, washed with distilled water, dried, and finally ground into a fine powder.

30 4.5 wt% SPSU solution in dimethylacetamide was used as binder for the catalyst layer. A slurry of 45 wt% Pt/C catalyst powder and 55 wt% polymer solution was mixed well and applied on to the supporting layer of the carbon paper by tape-casting. The platinum loading in the catalyst layer is 0.45 mg/cm². After drying, the electrode was impregnated with a mixed acid of 70 wt% phosphoric acid and 30 wt% trifluoroacetic acid.

35 An acid-doped blend polymer membrane of 75% PBI and 25% SPSU (sulfonation degree 44%) was used as the electrolyte. From the impregnated electrodes and acid-doped blend membrane, a membrane-electrode assembly was made by means of hot-press. The assembly was then placed in a test cell. At 190°C with hydrogen and oxygen, a cell performance of current density 0.88 A/cm² at cell voltage of 0.5 V was observed. When hydrogen containing 3 vol% CO was used as the fuel gas and oxygen as the oxidant, a current density

40 of 0.75 A/cm² at cell voltage of 0.5 V was observed.

45

Claims

5 Although this invention has been shown and described with respect to detailed embodiments hereof, it will be understood by those skilled in the art that many variations and modifications in form and detail thereof may be made without departing from the spirit and scope of the claimed invention. Therefore we claim:

- 10 1. A high temperature polymer membrane electrolyte fuel cell comprising a gas diffusion cathode for reducing an oxygen-containing oxidant gas, a gas diffusion anode for oxidizing a hydrogen-rich fuel gas, and a blend polymer membrane electrolyte. Said hydrogen-rich fuel gas contains at least 3 vol% carbon monoxide.
- 15 2. The high temperature polymer membrane electrolyte fuel cell of claim 1 wherein the blend polymer membrane electrolyte consists of polybenzimidazoles and one or more other thermoplastic resins doped with acids.
- 20 3. The blend polymer membrane electrolyte of claim 2 wherein said polybenzimidazole is poly(2,2'-m-(phenylene)-5,5''-bibenzimidazole). The composition of said polymer in the blend membranes is from 10 to 75 mol% PBI, preferably from 20 to 60 mol%.
- 25 4. The blend polymer membrane electrolyte of claim 2 wherein said thermoplastics are those miscible with polybenzimidazole from the group consisting of polyimides (PI), polyamides (PA), polyamideimides (PAI), polyetherimides (PEI), polyarylate (PAr), and poly(4-vinyl pyridine) (PVPy).
- 30 5. The blend polymer membrane electrolyte of claim 2 wherein said thermoplastics are immiscible with polybenzimidazole but can be converted into ionomers by e.g. sulfonation and become miscible with polybenzimidazoles because of the specific interaction.
- 35 6. The thermoplastics of claim 5 wherein said immiscible thermoplastic is polysulfone and said ionomer is sulfonated polysulfone. Said sulfonated polysulfone has a sulfonation degree between 5 and 80%, preferably from 15 to 60%.
- 40 7. The blend polymer membrane electrolyte of claim 2 being doped with an acid. Said acid is phosphoric acid or sulfuric acid of concentration preferably from 40 to 90 wt%.
8. The high temperature polymer membrane electrolyte fuel cell of claim 1 wherein the gas diffusion anode and cathode consists of a carbon backing substrate, a hydrophobic carbon supporting layer, and a catalyst layer. Said catalyst layer is cast from a slurry of catalyst powder and soluble polymer solution, dried at temperatures between 130-180°C for 3-15 minutes. Said catalyst powder consists of 10-20 wt% noble metal/alloys and 80-90 wt% carbon black.

9. The catalyst layer of claim 8 wherein the soluble polymer is used as binder and comprises the blend polymers described in claims 2-6.
- 5 10. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion cathode and anode are doped with a mixed acid consisting of 30-70 wt % nonvolatile acid and 30-70 wt% volatile acid. Said nonvolatile acid is phosphoric acid or sulfuric acid and said volatile acid is trifluoroacetic acid or acetic acid.
- 10 11. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion cathode and anode (claims 8-10) and the acid-doped polymer membrane electrolyte (claims 2-7) are assembled by hot-press.

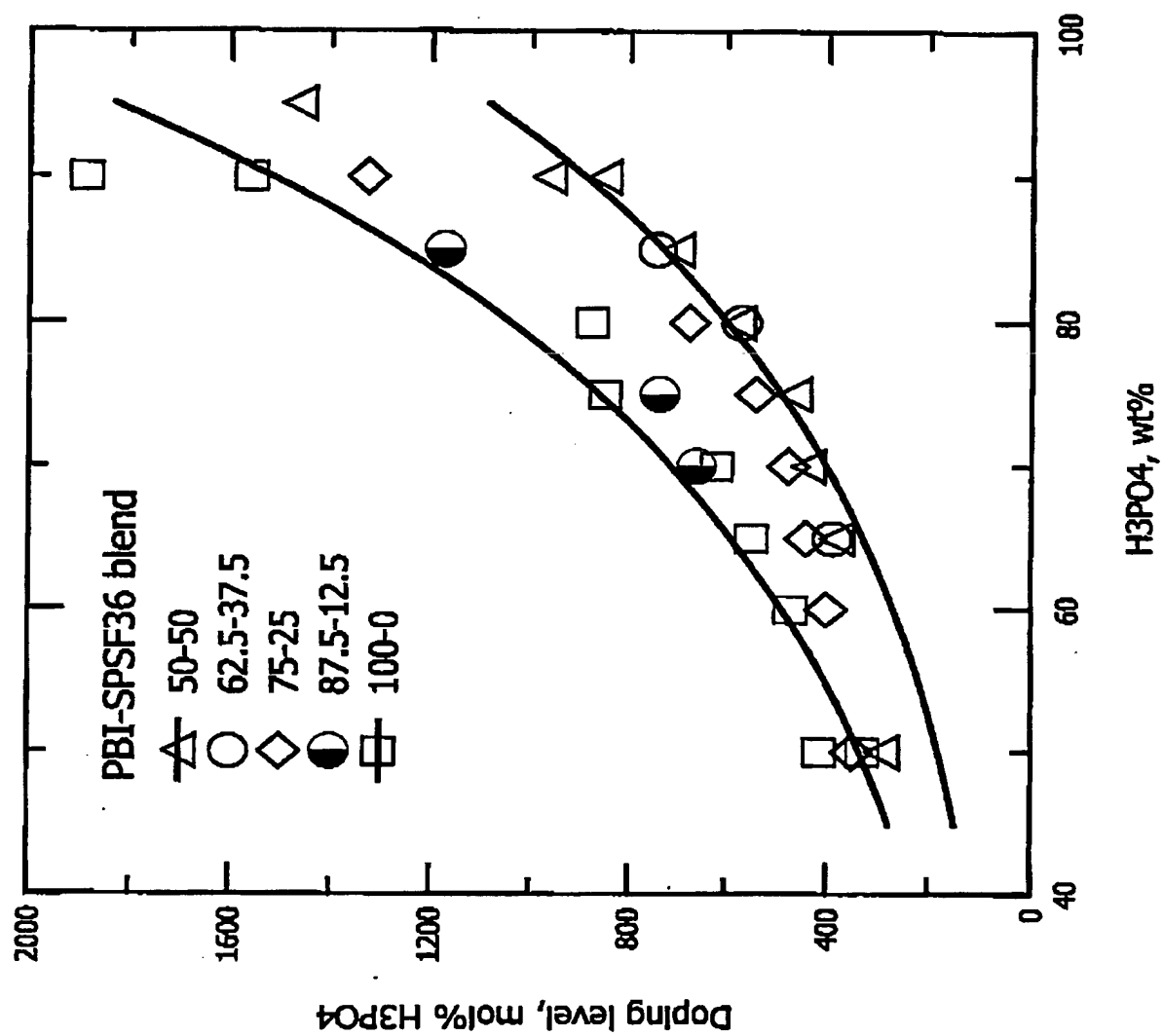


Fig. 1

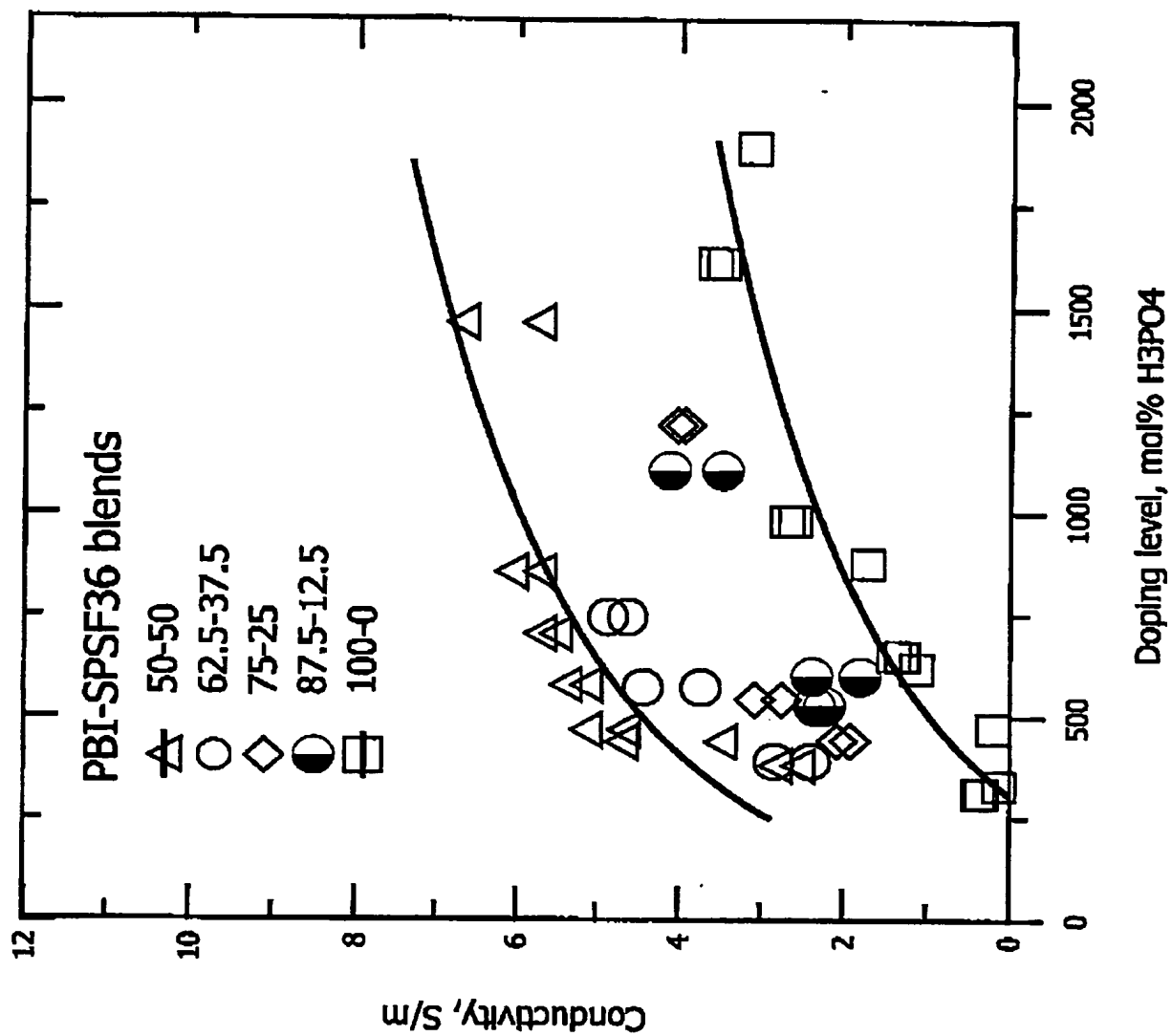


Fig. 2

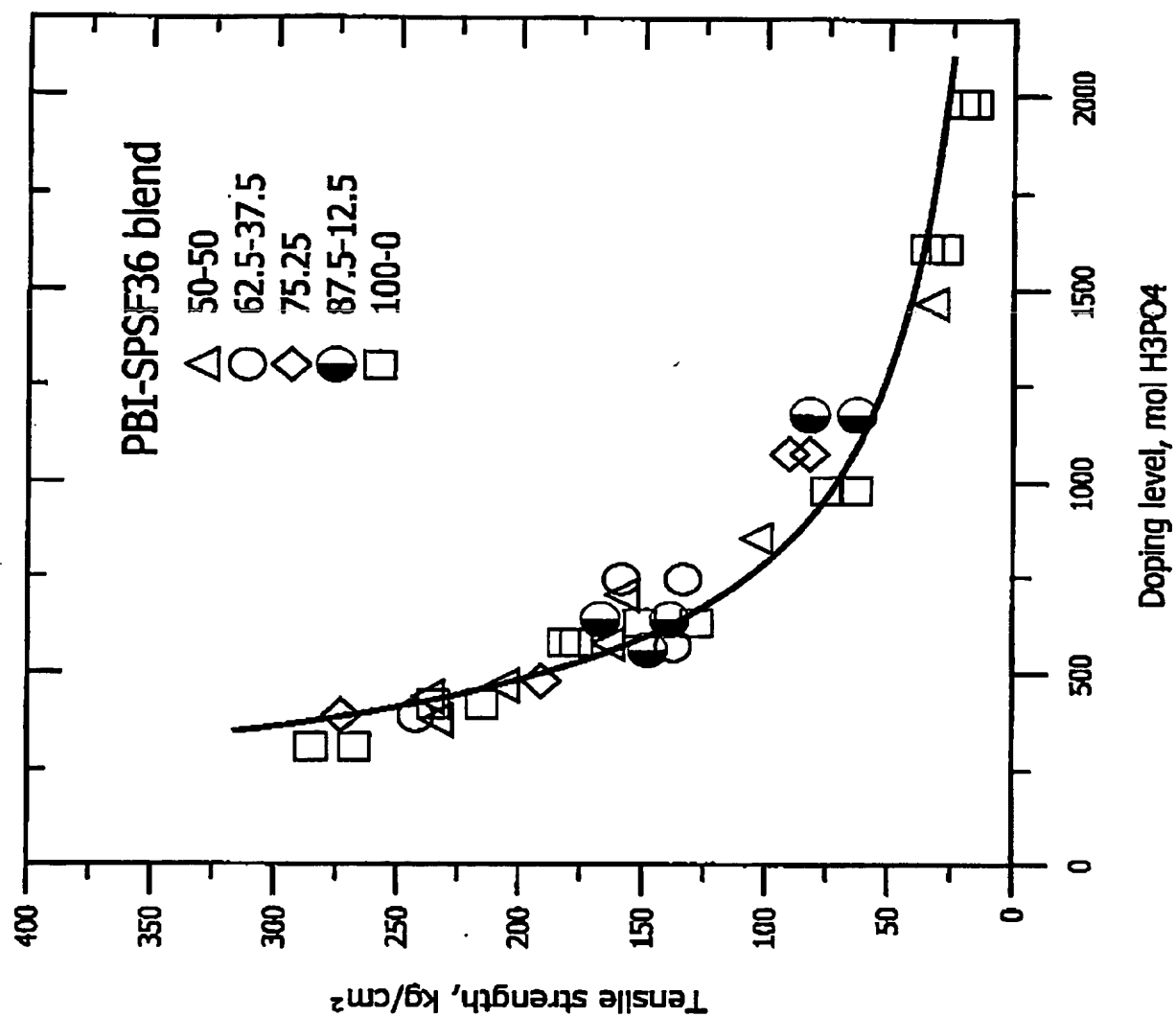


Fig. 3

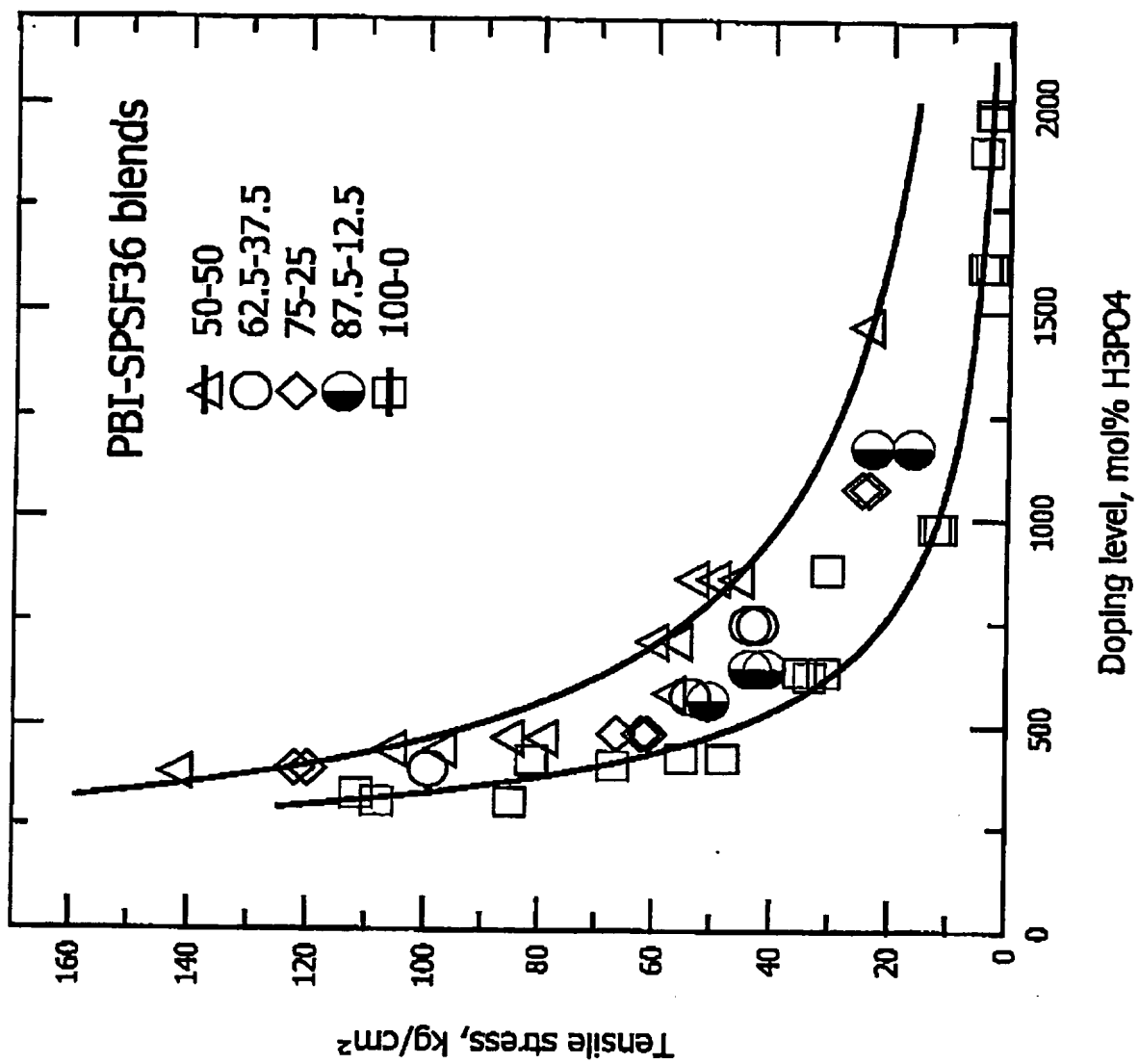


Fig. 4

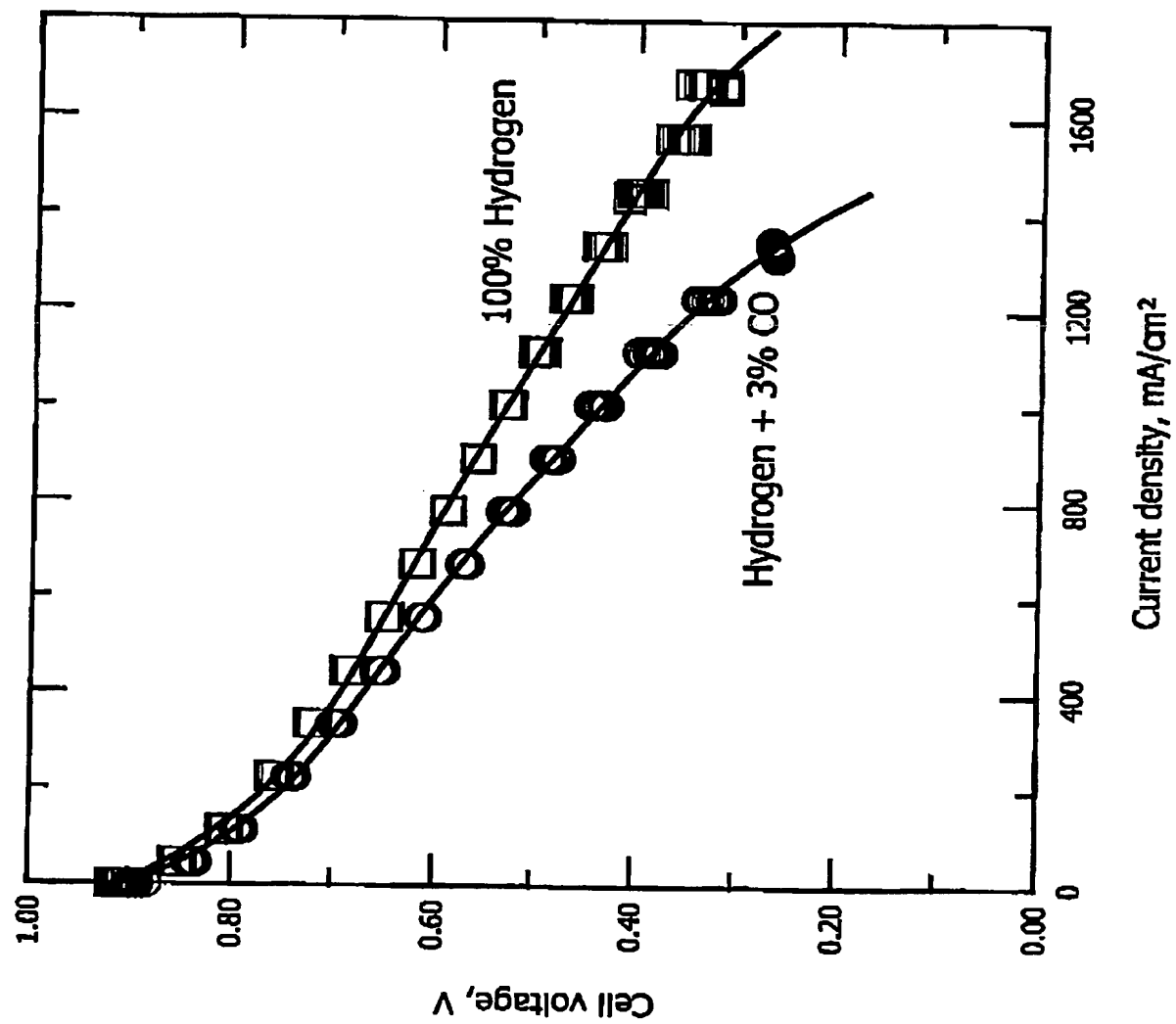


Fig. 5

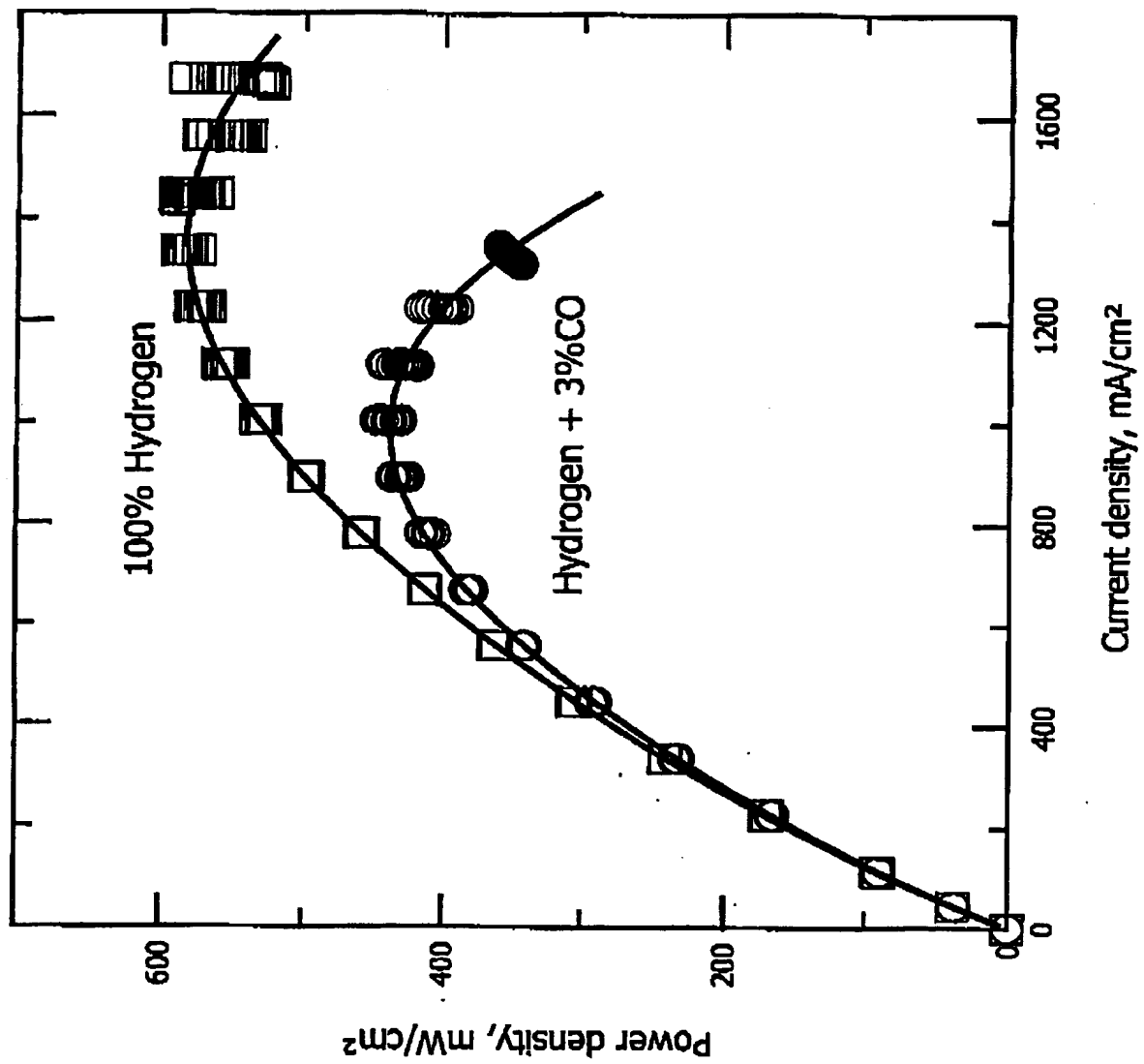


Fig. 6